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(54) Method of improving heat stability of pigmentable silicone elastomer.

(57) A method of improving the heat stability of silicone elastomers is disclosed. An improved pigmentable silicone elastomeric composition is produced by mixing a silicone elastomer composition having a vinyl radical content of from 0.01 to 0.1 percent by weight with a pretreated, white clay having a surface area of less than 50 m²/g, said surface containing olefinic unsaturated siloxy groups, and an organic peroxide vulcanizing agent. The improved silicone elastomeric composition is formed, then heated to vulcanize, to yield a silicone elastomer having improved resistance to the effects of elevated temperatures. The improved silicone elastomeric composition is also claimed. The improved silicone elastomeric composition can be pigmented.

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METHOD OF IMPROVING HEAT STABILITY OF
PIGMENTABLE SILICONE ELASTOMER

Background of the Invention

Field of the Invention

This invention relates to a method of improving the heat stability of pigmentable silicone elastomers that are catalyzed with organic peroxides and vulcanized with heat.

Description of the Prior Art

Elastomeric materials based upon

polyorganosiloxane polymers have found usefulness in part due to the resistance of the materials to the effects of elevated temperatures. In spite of the inherent heat stability of the polyorganosiloxane polymers, much work has been done to improve their heat stability.

The majority of the heat stability additives discovered are metallic oxides. Iron oxide is the most commonly used metallic oxide. Some metallic salts are also useful. Many of these additives are not useful when it is desired to impart color to the elastomer, because the metallic oxides and salts, per se, produce color in a silicone elastomer.



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United States Patent Number 3,341,489, issued September 12, 1967, to Simpson discloses the addition of certain olefinically unsaturated organosilicon materials such as vinyltriethoxysilane to an organopolysiloxane composition which is convertible to a cured, solid, elastic state. The resulting composition could be directly fabricated to valuable elastomeric products without the necessity of an extended post-cure.

A brochure entitled, "Silane Coupling Agents in Mineral-Reinforced Elastomers," published by Union Carbide Corporation, marked F-44715B, suggests that fillers such as calcined clays treated with vinyl functional silanes can be added to mineral-filled peroxide-cured elastomers, including silicone elastomers, to improve the mechanical and dynamic properties of elastomers. There is no teaching as to a method of improving the heat stability of silicone elastomers. Such treated inorganic fillers have been used in polyester resins, crosslinked polyethylene, ethylene-propylene rubber, and ethylene-propylene terpolymers to give products having improved physical properties.

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Summary of the Invention

A method of improving the heat stability of certain pigmentable silicone elastomeric compositions has been discovered. A silicone elastomeric composition having a vinyl radical content of from 0.01 to 0.1 percent by weight is mixed with a pretreated, white clay having a surface area of less than 50 m²/g, said surface containing olefinic unsaturated siloxy groups, and with an organic peroxide vulcanizing agent. The improved silicone elastomeric composition is formed and then vulcanized by heating. The cured silicone elastomer has improved heat resistance compared to the silicone elastomer stock without the addition of the pretreated, white clay.

It is an object of this invention to provide a method of improving the heat stability of specified silicone elastomers in a convenient and economical manner.

It is an object of this invention to provide a method of improving the heat stability of specified silicone elastomeric compositions in such a manner that the compositions can be pigmented to desired colors.

Description of the Invention

This invention relates to a method of improving the heat stability of a silicone elastomer comprising (A) mixing (1) 100 parts by weight of a mixture consisting essentially of a polydioryanosiloxane gum having organic

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radicals selected from the group consisting of methyl, vinyl, phenyl, and 3,3,3-trifluoropropyl, and from 10 to 100 parts by weight treated reinforcing silica filler, said mixture (1) having a vinyl radical content of from 0.01 to 0.1 percent by weight; (2) from 1 to 150 parts by weight of pretreated, white clay having a surface area of less than 50 m²/g, said surface having been treated so that the surface contains olefinic unsaturated siloxy groups; and (3) organic peroxide vulcanizing agent to yield an improved silicone elastomeric composition (B) forming the improved silicone elastomeric composition into a shape, and (C) heating the formed silicone elastomeric composition to an elevated temperature for a time sufficient to vulcanize the silicone composition, the vulcanized silicone elastomer having improved heat stability.

Silicone elastomers have become commercial products, in part, based upon their inherent resistance to the effects of exposure to elevated temperatures. Since their early commercialization, efforts have taken place to improve the heat stability of silicone elastomers. The method of this invention provides improved heat stability to certain silicone elastomers. This method has an added advantage in that it produces silicone elastomeric compositions which can be pigmented to a desired color in addition to having improved heat stability at least as economically as other known methods.

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The method of this invention, providing pigmentable silicone elastomers of improved heat stability, depends upon use of the specified silicone mixture (1) and the specified pretreated, white clay (2). The use of the clay (2) in conjunction with the specified silicone mixture (1) has yielded unexpected improvements in heat stability for the resulting silicone elastomer.

The silicone mixture (1) useful in this invention is commercially available in several embodiments. Those mixtures which contain the required vinyl radical content of from 0.01 to 0.1 percent by weight are operable. The mixtures contain polydiorganosiloxane gum having organic radicals selected from the group consisting of methyl, vinyl, phenyl, and 3,3,3-trifluoropropyl, said radicals being bonded to the silicon atoms of the polydiorganosiloxane. The polydiorganosiloxanes are commonly of a viscosity of from 1000 Pa·s up to and including non-flowing gums.

The mixture (1) also contains reinforcing silica filler to improve the physical strength of the polymer. Reinforcing silica fillers have a surface area of from 150 m²/g to greater than 400 m²/g. These reinforcing silica fillers are well known in the art and can be obtained commercially. The reinforcing silica filler can be treated or treated in situ during

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the manufacture of the mixture. The treated reinforcing silica fillers can be treated by any one of the conventional methods described in the prior art, wherein the treating agents include organosilanes, organosiloxanes, and silazanes. Methods of preparing treated reinforcing silica are disclosed in U.S. Patent No. 3,122,516 issued February 25, 1969 to Polmanteer; U. S. Patent No. 3,334,062, issued August 1, 1967 to Brown and Hyde; U.S. Patent No. 3,635,743, issued January 18, 1974 to Smith; and U.S. Patent No. 3,624,023, issued November 30, 1977, to Hartage, which show the preparation of treated silica fillers. The amount of reinforcing filler can vary from 10 to as much as 100 parts by weight with the preferred amount varying between 15 to 75 parts by weight per 100 parts by weight of the polydiorganosiloxane.

If the reinforcing silica filler is not treated as described above, it is necessary to treat the reinforcing silica in situ during the mixing step to prevent reaction between the polydiorganosiloxane gum and the reinforcing filler. This reaction produces a mixture that becomes too stiff to be workable, a phenomenon known as crepe-hardening. The reinforcing silica can be treated in situ by adding anticrepe-hardening agents during the mixing of the



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composition. During the preparation of mixture (1), the mixture may be heated during the mixing step to improve the reaction between the hydroxyl radicals on the surface of the reinforcing silica and the anticrepe-hardening agents. Useful anticrepe-hardening agents are well known in the art. They include low molecular weight silanes, siloxanes and silazanes. Short chain siloxanes, typically endblocked with hydroxyl or alkoxy groups so that they may react with the hydroxyl groups present on the surface of the reinforcing filler, are often used. The organic radicals present in the anticrepe-hardening agents are the same as those found in polydiorganosiloxane gum.

The silicone elastomeric composition may also contain minor amounts of additive to improve the properties such as handling, compression set, oil resistance, etc. The additives should be those which do not impart color to the composition unless the additive imparts a color which is desired.

The pigmentable silicone elastomeric composition may be composed of a single polydiorganosiloxane gum or a mixture of different gums. The composition may also contain a single reinforcing silica filler or a mixture of reinforcing silica fillers.



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The mixture (1) or combination of mixtures is required to have a vinyl radical content of from 0.01 to 0.1 percent by weight. The vinyl radicals may be present in the polydiorganosiloxane, the antirepe-hardening agent, on the surface of the reinforcing filler, or in other additives used in the mixture. The preferred vinyl radical content is from 0.025 to 0.1 percent by weight.

The other critical ingredient present in the silicone elastomeric composition used in the method of this invention is a pretreated, white clay having a surface area of less than 50 m²/g. The surface of the clay has been treated so that it contains olefinic unsaturated siloxy groups.

The surface area of fillers normally varies with the particle size and is useful in describing the physical nature and size of small particles. As the particles become smaller, the surface area increases. A kaolin clay of an average particle size of 4.5 micrometres has a surface area of 6 to 7 m²/g and clays of 0.2 micrometres average particle size have surface areas varying from about 12 to 20 m²/g depending upon how much the particles are agglomerated.

The clays useful in this invention are those pretreated clays which do not color the silicone elastomeric composition and which permits the silicone elastomeric composition to be pigmented or colored to the desired hue. Those clays which are themselves



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highly colored are not suitable because their use in the silicone elastomeric composition does not permit pigmenting to a desired color unless the desired color was of a similar hue to that produced by the colored clay.

Suitable clays are the aluminum silicate minerals which are commercially mined and refined for use as fillers in paints, plastics and elastomers. Clays are further defined as illite, kaolinite, and montmorillonite, all of which are complex aluminum silicate minerals. Kaolinite or kaolin clay is a preferred clay because it is readily available in a white form. For purposes of this invention, "white" is to be regarded as the absence of a hue or tint of sufficient strength to prevent the further pigmenting of the silicone elastomeric composition to a desired color. When a suitable clay is mixed into the silicone elastomeric composition, the composition may be changed to a cream color, but it is still easily pigmented as the clay has low hiding power and low tint strength.

The white clay having the required surface area is pretreated before use in the method of this invention so that the surface of the clay contains olefinic unsaturated siloxy groups. The most common siloxy groups are the vinyl siloxy group and the

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methacryloxy group. Pretreated white clays having the required surface area and surface treatment are commercially available. A typical pretreated clay is a calcined kaolin having an average particle size of 0.8 micrometres that has been treated with vinyl-tris(beta-methoxyethoxy)silane in a water slurry, then dried to yield a vinylsiloxy treated kaolin.

As little as 1 part by weight of pretreated, white clay is useful in improving the heat stability of the silicone elastomer of this invention. Increasing the amount of pretreated, white clay to 10 or 20 parts by weight of clay to 100 parts by weight of mixture (1) further improves the heat stability. When 110 parts of pretreated, white clay was added to a mixture (1) falling within the requirements of this invention, the heat stability of the resulting silicone elastomer was improved over a similar formulation made with an untreated ground quartz filler (commonly used in silicone elastomers) falling outside the scope of this invention. The retention of physical properties was not as high in the case of this composition using a large amount of pretreated, white clay as when a smaller amount was used. It is to be noted, however, that the initial properties of the compositions are also different.

The preferred amount of pretreated, white clay to be used in the method of this invention is dependent upon the requirement of the cured silicone

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elastomer, as well as the other ingredients used in the silane elastomeric composition. As more clay is added, for instance, the durometer of the cured silicone elastomer rises. If there is a specified durometer in the lower ranges, the amount of filler in the silicone elastomer will have to be at a lower level than if the specified durometer were in the higher ranges. Such effects are well known in the art and the optimum amount of the various ingredients is easily determined by simple experimentation.

The compositions of this invention, containing the pretreated, white clay used in this invention, can be pigmented to a desired or required color because the clay useful in this invention does not in itself color the composition. Many of the previously known methods of improving the heat stability of silicone elastomers relied upon the addition of materials which strongly colored the composition so that the choice of colors that could be produced was severely limited. The method of this invention thus produces a composition having both improved heat stability and pigmentability through the use of a commercially obtainable and low cost ingredient. The combination of the specified mixture (1) and the pretreated, white clay (2) has been unexpectedly found to provide these advantages.

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Inorganic extending filler which has not been treated can optionally be added to the composition used in this method. The use of untreated inorganic extending filler will dilute the effect of using the pretreated, white clay so the relative amounts of clay and untreated inorganic extending filler must be judged by their effect upon the properties of the cured silicone elastomer. Inorganic extending fillers useful in silicone elastomers are well known in the art.

The compositions of this invention can be pigmented with the well-known pigments available for use with silicone elastomer. The pigments are heat-stable and have little or no effect upon the properties of the vulcanized silicone elastomer. The pigments are normally inorganic oxides or salts which are finely dispersed in a silicone polymer to give a masterbatch which can be easily dispersed during the mixing of the silicone elastomeric composition.

The silicone elastomeric composition contains an organic peroxide vulcanizing agent suitable for vulcanizing the polydioryanosiloxane in the silicone elastomeric mixture. Since the polydioryanosiloxane contains vinyl radicals, it can be vulcanized with either "non-vinyl specific" or "vinyl specific" organic peroxides. Representative of the vinyl specific organic peroxides are ditertiary-butylperoxide and 2,5-bis-(tertbutylperoxy)-2,5-dimethylhexane. Representative of the non-vinyl

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specific peroxides are benzoylperoxide, dicumylperoxide, and 2,4-dichlorobenzoylperoxide. All these organic peroxide vulcanizing agents and their properties are well known in the art. The properties of the cured silicone elastomer can be altered by the type and amount of vulcanizing agent used to cure the composition. Typical changes due to such choices are well recognized in the art. The vulcanizing agent is generally present in amounts from 0.1 to 5 parts by weight per 100 parts by weight of silicone elastomer base, preferably from 0.5 to 2.0 parts by weight.

The first step of the method of this invention is mixing the mixture (1), pretreated, white clay (2), organic peroxide vulcanizing agent (3), and optional ingredients. Methods of mixing that are common in the silicone elastomer art and which are suitable for this invention include mixing with a dough mixer, a rubber compounding mill, or with a Banbury mixer. The order of mixing is not critical. Ordinarily, the mixture (1) is placed in the mixer, the clay (2) and other additives are added and mixed until homogeneous, then the vulcanizing agent is added and mixed until homogeneous. When pigment is used to color the silicone elastomeric composition to a desired color, the pigment should be added to the mixing procedure along with the clay (2) and other additives so that it is well distributed throughout the mixture, resulting in a uniform color.

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After the improved silicone elastomeric composition is prepared in the mixing step, the composition is formed to the desired shape. The composition can be formed into a shape by any of the conventional well known methods of forming elastomeric curable compositions such as press molding, injection molding, calendaring, and extruding, both supported and unsupported.

The shaped composition is then cured or vulcanized by heating to an elevated temperature for a time sufficient to cause decomposition of the organic peroxide vulcanizing agent and subsequent crosslinking of the polydiorganosiloxane. The time and temperature necessary to cause vulcanization of the stock are dependent upon the organic peroxide vulcanizing agent chosen, the method of heating, the method of forming the composition into a shape, and the thickness of the part. The temperature that is appropriate for a given set of conditions is well known in the silicone elastomer art. Typical temperatures are from 110°C to 175°C for molding operations to as high as 300°C for the ovens used in continuous hot air vulcanization operations.

The cured silicone elastomers produced by following the method of this invention have improved heat stability when compared to similar cured silicone elastomers produced in a similar manner, but not including the pretreated, white clay used in the method of this invention. It is completely unexpected that the inclusion of as little as 1 part by weight



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pretreated, white clay in 100 parts by weight of silicone elastomeric composition would significantly improve the resistance of the stock to change in physical properties upon exposure to heat. The amounts of pretreated, white clay that are useful and the availability of the pretreated, white clay makes the method of this invention a particularly desirable method of improving the heat stability of silicone elastomers. The method is additionally useful in that the silicone elastomers can be of any desired or required color.

The silicone elastomers produced by the method of this invention are suitable for uses customarily known for silicone elastomers such as molded parts for high temperature applications, gaskets, O-rings, diaphragms, tubing, and insulated electrical wiring. Insulated electrical wiring can be easily colored to conform to the required color codes.

The following examples are included for illustrative purposes only and should not be construed as limiting the invention which is properly delineated by the appended claims. All parts are parts by weight.

Example 1

This example shows the improvement in heat aging obtained when a minor amount of pretreated, white clay is present in a silicone elastomeric composition.

Mixtures were prepared on a two-roll rubber mill by mixing 100 parts of a commercial silicone mixture with various amounts of pretreated, white clay as shown in Table 1. The commercial silicone



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elastomeric mixture contained a dimethylvinylsiloxyl endblocked polydiorganosiloxane gum having both dimethylsiloxyl units and methylvinylsiloxyl units in an amount such that the gum averaged about 0.09 percent by weight vinyl radical, hydroxyl endblocked polydimethylsiloxane fluid as an antirepe-hardening agent, and reinforcing silica filler having a surface area of about 250 m²/g. The mixture contained approximately 0.07 percent by weight vinyl radical.

The pretreated, white clay was a calcined kaolin clay which had been treated with approximately 1 percent by weight of vinyl-tris(beta-methoxyethoxy)silane. Thus the clay had a maximum of about 0.1 percent by weight of vinyl radical in the form of vinyl siloxyl groups bonded to its surface. The treated kaolin had an average particle size of about 0.81 micrometres.

Each mixture was catalyzed with either one part of catalyst A (50 percent active powder of 2,5-bis-(tert-butyl peroxy)-2,5-dimethylhexane, a vinyl specific catalyst) or 1.5 parts of catalyst B (50 percent active paste of 2,4 dichlorobenzoyl peroxide, a non-vinyl specific catalyst) as shown in Table 1.

Each catalyzed mixture was pressed into a test slab approximately 2.54 mm thick and cured for 10 minutes at 171°C in the case of catalyst A, or 5 minutes at 116°C in the case of catalyst B. After

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press curing, the slabs were cut into test pieces and tested according to ASTM D2240 for durometer, and ASTM D412 for tensile strength and percent elongation at break. The test results are shown in Table 1.

Additional test pieces were heat aged in an air circulating oven for 24 hours at 250°C, cooled, and tested as above. The change in properties due to the heat aging was then calculated. These results are shown in Table 1.

The change in physical properties caused by the heat aging of the test pieces is much less in those containing a small amount of pretreated, white clay than in those test pieces without the added pretreated, white clay. This improvement in heat aging is unexpected since only a small amount of pretreated, white clay was added. The total filler content of the cured elastomer was not changed significantly. The amount of vinyl radical present on the pretreated, white clay was only about 14 percent or 28 percent of the vinyl present in the base, depending upon the amount of pretreated, white clay used. The total amount of vinyl radical was not changed significantly.

Example 2

The previous Example was repeated using a different commercial silicone mixture. The mixture of this Example was the same as in Example 1 except it contained a higher amount of reinforcing filler and anticrepe-hardening agent so that the mixture contained about 0.064 percent by weight vinyl radical.

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Compositions were prepared and tested as in Example 1. The test results shown in Table 2 show that the addition of minor amounts of the pretreated, white clay again improved the resistance to physical property change caused by heat aging.

Example 3

The effect of using a clay similar to that of Example 2 but without treatment was evaluated.

The filler was a calcined kaolin clay, further identified as anhydrous aluminum silicate, $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ having an average particle size of about 0.8 micrometre with at least 70 percent by weight of the particles being less than 2 micrometres.

The mixtures of Example 2 were repeated, except the untreated clay described above was used in place of the pretreated, white clay. Preparation of samples and testing was as in Example 1. The results are shown in Table 3.

The untreated clay did not improve the resistance to physical property change caused by heat aging in the manner or to the degree as did the pretreated, white clay of this invention.

Example 4

The effect of adding a large quantity of pretreated, white clay and untreated extending filler was evaluated.

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The mixture of Example 1 was mixed with 110 parts of the pretreated, white clay described in Example 1. The mixture of Example 1 was also mixed with 110 parts of ground quartz filler having a nominal particle size of 5 micrometres. This is a commercial extending filler commonly used in silicone elastomer. The mixtures were prepared and tested as in Example 1. The results are shown in Table 4.

The change in properties due to the effect of heat aging is much greater with the untreated extending filler than with the pretreated, white clay.

Example 5

The use of pretreated, white clay in a mixture similar to that of Example 1, but containing a higher amount of reinforcing silica filler and anticrepe-hardening agent, was evaluated. The mixture used in this experiment contained about 0.05 percent by weight vinyl radical.

The mixture was mixed with the amount of pretreated, white clay of Example 1 as shown in Table 5 and one part of either catalyst A or B as shown. The compositions were prepared and tested as in Example 1.

The results show that the addition of a minor amount of pretreated, white clay improved the resistance to physical property change caused by heat aging.

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Example 6

This example shows the effect of pretreated, white clay added to a mixture having a vinyl radical content of greater than 0.1 percent by weight, an amount outside the claims of this invention.

This mixture contained a dimethylvinylsiloxyl endblocked polydimethylsiloxane gum, the gum being approximately 0.044 percent by weight vinyl radical. The gum was reinforced with a fume silica having a surface area of about 250 m²/g the surface being treated with trimethylsiloxyl groups. Also included was a dimethylvinylsiloxyl endblocked polydiorganosiloxane fluid having both dimethylsiloxyl units and methylvinylsiloxyl units in an amount such that the fluid was 7.55 percent by weight vinyl radicals. The mixture contained approximately 0.15 percent by weight vinyl radical.

Compositions were prepared of the above base and the pretreated, white clay of Example 1 in the amount shown in Table 6 in combination with catalyst A and B of Example 1. The compositions were prepared and tested as in Example 1. The results in Table 6 show that the pretreated, white clay was not effective in improving the heat stability of this comparative mixture.

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Example 7

This example shows the effect of pretreated, white clay in another mixture having a vinyl radical content of greater than 0.1 percent by weight, an amount outside the claims of this invention.

The mixture of this example contained the same dimethylvinylsiloxy endblocked polydiorganosiloxane gum of Example 1. The reinforcing filler was a fume silica having a surface area of about 250 m²/g. The anticrepe-hardening agent was a mixture of a hydroxyl endblocked polymethylphenylsiloxane fluid and a hydroxyl endblocked polymethylvinylsiloxane fluid. The mixture contained approximately 0.2 percent by weight vinyl radical.

Compositions were prepared of the above mixture and the pretreated, white clay of Example 1 in the amounts shown in Table 7 in combination with catalyst A and B of Example 1. The compositions were prepared and tested as in Example 1. The results in Table 7 show that the pretreated, white clay was not effective in improving the heat stability of this composition, when catalyst A was used. With catalyst B, it appears that the stock did not cure properly when pressed, but cured during the heat aging.

Table 1

| | | | | | |
|---|------|------|------|------|------|
| Pretreated, white clay, parts Catalyst | None | 10 | 20 | None | 10 |
| | A | A | A | B | B |
| <u>After press cure</u> | | | | | |
| Durometer, Shore A | 38 | 41 | 46 | 40 | 43 |
| Tensile strength, MPa | 4.75 | 5.41 | 5.86 | 4.86 | 5.37 |
| Elongation, percent | 485 | 440 | 370 | 410 | 360 |
| <u>After heat aging 24 hours at 250°C</u> | | | | | |
| Durometer, Shore A | 52 | 40 | 45 | 45 | 42 |
| Tensile strength, MPa | 2.58 | 4.96 | 5.72 | 2.72 | 6.20 |
| Elongation, percent | 85 | 340 | 340 | 120 | 330 |
| <u>Change in properties due to heat aging</u> | | | | | |
| Durometer, Shore A | +14 | -1 | -1 | +5 | -1 |
| Tensile strength, percent | -46 | -8 | -2 | -44 | +15 |
| Elongation, percent | -83 | -23 | -9 | -71 | -8 |

Table 2

Pretreated, white
clay, parts
Catalyst

| None | 1 | 10 | 20 | None | 10 | 20 |
|------|---|----|----|------|----|----|
| A | A | A | A | B | B | B |

After press cure

| | | | | | | |
|-----------------------|------|------|------|------|------|------|
| Durometer, Shore A | 41 | 42 | 45 | 48 | 40 | 44 |
| Tensile strength, MPa | 7.41 | 7.85 | 7.91 | 7.72 | 6.20 | 6.13 |
| Elongation, percent | 520 | 530 | 470 | 390 | 430 | 350 |

After heating aging 24 hours at 250°C

| | | | | | | |
|-----------------------|------|------|------|------|------|------|
| Durometer, Shore A | 51 | 44 | 46 | 52 | 45 | 52 |
| Tensile strength, MPa | 3.31 | 4.34 | 7.06 | 7.03 | 7.44 | 7.03 |
| Elongation, percent | 150 | 240 | 410 | 360 | 425 | 250 |

Change in properties due to heat aging

| | | | | | | |
|---------------------------|-----|-----|-----|----|-----|-----|
| Durometer, Shore A | +10 | +2 | +1 | +4 | +3 | +8 |
| Tensile strength, percent | -55 | -45 | -4 | -9 | +20 | +14 |
| Elongation, percent | -71 | -55 | -13 | -8 | -1 | 0 |

Table 3

| | | | |
|---|------|------|------|
| Untreated Clay, parts | None | 10 | 20 |
| Catalyst | A | A | A |
| <u>After press cure</u> | | | |
| Durometer, Shore A | 40 | 40 | 32 |
| Tensile Strength, MPa | 6.76 | 6.41 | 6.13 |
| Elongation, percent | 570 | 590 | 820 |
| <u>After heat aging 24 hours at 250°C</u> | | | |
| Durometer, Shore A | 60 | 54 | 55 |
| Tensile Strength, MPa | 1.03 | 1.56 | 1.48 |
| Elongation, percent | 30 | 200 | 100 |
| <u>Change in properties due to heat aging</u> | | | |
| Durometer, Shore A | +20 | +14 | +23 |
| Tensile Strength, percent | -85 | -71 | -76 |
| Elongation, percent | -95 | -66 | -88 |

Table 4

| | | | | |
|-----------------------------------|-----|-----|-----|-----|
| Pretreated, white Clay, parts | 110 | - | 110 | - |
| Untreated Extending Filler, parts | - | 110 | - | 110 |
| Catalyst | A | A | B | B |

After press cure

| | | | | |
|-----------------------|------|------|------|------|
| Durometer, Shore A | 76 | 60 | 73 | 63 |
| Tensile strength, MPa | 6.20 | 3.62 | 6.48 | 3.86 |
| Elongation, percent | 110 | 365 | 120 | 205 |

After heat aging 24 hours at 250°C

| | | | | |
|-----------------------|------|------|------|------|
| Durometer, Shore A | 80 | 65 | 78 | 65 |
| Tensile strength, MPa | 5.00 | 5.99 | 5.37 | 5.72 |
| Elongation, percent | 80 | 155 | 100 | 120 |

Change in properties due to heat aging

| | | | | |
|---------------------------|-----|-----|-----|-----|
| Durometer, Shore A | +4 | +5 | +5 | +2 |
| Tensile strength, percent | -19 | +66 | -17 | +48 |
| Elongation, percent | -27 | -58 | -17 | -42 |

Table 5

| Pretreated, white Clay, parts Catalyst | None | | 10 | | None | | 10 | |
|---|------|--|------|--|------|--|------|--|
| | A | | A | | B | | B | |
| <u>After press cure</u> | | | | | | | | |
| Durometer, Shore A | 61 | | 65 | | 59 | | 65 | |
| Tensile strength, MPa | 7.41 | | 7.03 | | 7.96 | | 8.10 | |
| Elongation, percent | 460 | | 380 | | 420 | | 380 | |
| <u>After heat aging 24 hours at 250°C</u> | | | | | | | | |
| Durometer, Shore A | 93 | | 82 | | 83 | | 80 | |
| Tensile strength, MPa | 3.10 | | 5.68 | | 4.07 | | 6.55 | |
| Elongation, percent | 40 | | 190 | | 50 | | 190 | |
| <u>Change in properties due to heat aging</u> | | | | | | | | |
| Durometer, Shore A | +32 | | +17 | | +24 | | +15 | |
| Tensile strength, percent | -58 | | -19 | | -49 | | -19 | |
| Elongation, percent | -91 | | -50 | | -88 | | -50 | |

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Table 6

| Pretreated, white clay, parts Catalyst | None | | 10 | |
|--|------|---|----|---|
| | A | B | A | B |

After press cure

| | | | | |
|-----------------------|------|------|------|------|
| Durometer, Shore A | 45 | 48 | 45 | 49 |
| Tensile strength, MPa | 9.47 | 9.47 | 9.30 | 8.27 |
| Elongation, percent | 800 | 790 | 725 | 630 |

After heat aging 24 hours at 250°C

| | | | | |
|-----------------------|------|------|------|------|
| Durometer, Shore A | 63 | 63 | 54 | 61 |
| Tensile strength, MPa | 4.93 | 5.27 | 6.70 | 6.37 |
| Elongation, percent | 240 | 300 | 340 | 230 |

Change in properties due to heat aging

| | | | | |
|---------------------------|-----|-----|-----|-----|
| Durometer, Shore A | +18 | +15 | + 9 | +12 |
| Tensile strength, percent | -48 | -44 | -28 | -23 |
| Elongation, percent | -70 | -62 | -53 | -64 |

Table 7

Pretreated, white clay, parts
Catalyst

None 10 20 None 10 20

A A A B B

After press cure

Durometer, Shore A 39 41 48 34 36 40
Tensile strength, MPa 3.03 4.34 5.86 3.24 3.48 3.24
Elongation, percent 260 260 260 335 290 220

After heat aging 24 hours at 250°C

Durometer, Shore A 35 41 41 34 28 32
Tensile strength, MPa 2.10 2.96 3.93 2.14 4.62 5.10
Elongation, percent 160 160 240 155 430 420

Change in properties due to heat aging

Durometer, Shore A -4 0 -7 0 -8 -8
Tensile strength, percent -31 -32 -33 -34 +33 +84
Elongation, percent -30 -38 -8 -54 +48 +90

Claims:

1. Method of improving the heat stability of a silicone elastomer characterized by:

- (A) mixing (1) 100 parts by weight of a mixture consisting essentially of a polydiorgano-siloxane gum having organic radicals selected from the group consisting of methyl, vinyl, phenyl, and 3,3,3-trifluoropropyl, and from 10 to 100 parts by weight treated reinforcing silica filler, said mixture (1) having a vinyl radical content of from 0.01 to 0.1 percent by weight; (2) from 1 to 150 parts by weight of pretreated, white clay having a surface area of less than 50 m²/g, said surface having been treated so that the surface contains olefinic unsaturated siloxy groups; and (3) organic peroxide vulcanizing agent to yield an improved silicone elastomeric composition
- (B) forming the improved silicone elastomeric composition into a shape, and
- (C) heating the formed silicone elastomeric composition to an elevated temperature for a time sufficient to vulcanize the silicone elastomeric composition, the vulcanized silicone elastomer having improved heat stability.

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2. The method of claim 1 in which the mixture (1) is heated before the addition of the pretreated, white clay.

3. The method of claim 1 in which the mixture (1) has a vinyl radical content of from 0.025 to 0.1 percent by weight.

4. The method of claim 3 in which the pretreated, white clay is a kaolin clay having a surface containing vinylsiloxo groups and having an average particle size of less than 5 micrometres.

5. A silicone elastomeric composition comprising the product obtained by mixing

- (1) 100 parts by weight of a mixture consisting essentially of a polydioryanosiloxane gum having organic radicals selected from the group consisting of methyl, vinyl, phenyl, and 3,3,3-trifluoropropyl, and from 10 to 100 parts by weight of treated reinforcing silica filler, said mixture (1) having a vinyl radical content of from 0.01 to 0.1 percent by weight, and characterized by

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- (2) from 1 to 150 parts by weight of pretreated, white clay having a surface area of less than $50 \text{ m}^2/\text{g}$, said surface having been treated so that the surface contains olefinic unsaturated siloxy groups; and
- (3) organic peroxide vulcanizing agent, to yield a silicone elastomeric composition which, when vulcanized, has improved heat stability.

6. The composition of claim 5 in which the mixture (1) has a vinyl radical content of from 0.025 to 0.1 percent by weight.

7. The composition of claim 6 in which the pretreated, white clay is a kaolin clay having a surface containing vinylsiloxy groups and having an average particle size of less than 5 micrometres.

8. The composition of claim 5 in which there is also present a heat stable pigment.

(19)



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(54) Method of improving heat stability of pigmentable silicone elastomer.

(57) A method for the heat stabilisation of silicone elastomers is disclosed. A pigmentable silicone elastomeric composition is produced by mixing a silicone elastomer composition having a vinyl radical content of from 0.01 to 0.1 percent by weight with a pretreated, white clay having a surface area of less than 50 m²/g, said surface containing olefinic unsaturated siloxy groups, and an organic peroxide vulcanizing agent. The silicone elastomeric composition is formed, then heated to vulcanize, to yield a silicone elastomer having resistance to the effects of elevated temperatures. The silicone elastomeric composition is also claimed. The silicone elastomeric composition can be pigmented.

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0057084

Application number

EP 82 30 0301.7

| DOCUMENTS CONSIDERED TO BE RELEVANT | | | CLASSIFICATION OF THE APPLICATION (Int. Cl. 7) |
|---|---|----------------------------------|---|
| Category | Citation of document with indication, where appropriate, of relevant passages | Relevant to claim | |
| Y | XEROX DISCLOSURE JOURNAL Vol. 5, No. 5, September/October 1980 J.A. LENTZ et al. "Filler Treatments for Thermally Conductive Silicone Elastomers" * pages 493 to 494 * | 1,4,7 | C 08 L 83/04 C 08 G 77/20 C 08 K 3/34 C 08 K 9/06 C 08 J 3/24 |
| Y | "Encyclopaedia of Polymer Science and Technology", Vol. 12 1970, INTERSCIENCE PUBLISHERS, New York pages 534 to 540 * page 534, line 43 to page 535, line 48; page 536, table 13; page 537, lines 37 to 43 * | 1,4,7 | C 08 G 77/20 C 08 J 3/24 C 08 K 3/34 C 08 K 9/06 C 08 L 83/04 |
| A | * page 537, line 37 to page 539, line 14; page 540, lines 8 to 20 * | 2,8 | |
| A | GB - A - 957 108 (IMPERIAL CHEMICAL INDUSTRIES LTD.) * claims 1, 4; page 1, line 90 to page 2, line 8 * | 1,3,6 | |
| A | DE - A - 2 237 459 (RAYCHEM CORP.) * claims 1, 6 to 13; page 5, line 23 to page 6, line 6; page 7, line 9 to page 8, line 13; page 12, line 18 to page 14, line 19 * | 1,3-6, 8 | |
| | | | <p>TECHNICAL FIELDS SEARCHED (Int.Cl. 7)</p> <p>CATEGORY OF CITED DOCUMENTS</p> <p>X: particularly relevant if taken alone Y: particularly relevant if combined with another document of the same category A: technological background O: non-written disclosure P: intermediate document T: theory or principle underlying the invention E: earlier patent document, but published on, or after the filing date D: document cited in the application L: document cited for other reasons</p> |
| <p><input checked="" type="checkbox"/> The present search report has been drawn up for all claims</p> | | | <p>&: member of the same patent family, corresponding document</p> |
| Place of search | | Date of completion of the search | Examiner |
| Berlin | | 21-05-1982 | IDEZ |



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|-------------------------------------|---|-------------------|--|
| Category | Citation of document with indication, where appropriate, of relevant passages | Relevant to claim | |
| D,A | <p>US - A - 3 341 489 (V.G. SIMPSON)</p> <p>* claims 1, 2, 9; column 2, lines 47 to 58; column 3, line 57 to column 4, line 66 *</p> <p>-----</p> | 1,3,5,6,8 | |
| | | | TECHNICAL FIELDS SEARCHED (Int. Cl.) |
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